



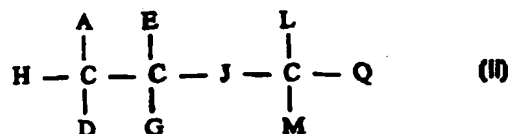
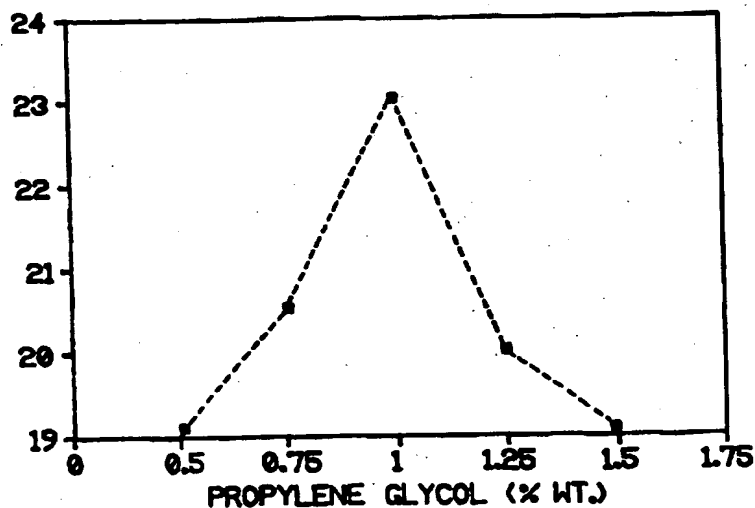
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: GLASS CLEANER WITH ENHANCED ANTI-STREAKING PROPERTIES

## (57) Abstract

An aqueous glass cleaning composition with optimal anti-streaking properties contains a nonvolatile organic ether having the formula:  $R_1-O-R_2$ , wherein  $R_1$  is a  $C_1-C_8$  linear, branched or cyclic alkyl or alkenyl optionally substituted with -OH, and  $R_2$  is a  $C_1-C_6$  linear, branched or cyclic alkyl or alkenyl substituted with -OH; and an anti-streaking alcohol having formula (II) wherein A, D, E, G, L and M are independently -H, -CH<sub>3</sub>, -OH or -CH<sub>2</sub>OH; J is a single bond or -O-; and Q is -H or a straight chain  $C_1-C_3$  alkyl optionally substituted with -OH.

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## GLASS CLEANER WITH ENHANCED ANTI-STREAKING PROPERTIES

5

### Technical Field

The present invention relates to compositions for cleaning glass surfaces. In particular, the present invention relates to improved anti-streaking glass cleaning compositions.

10

### Background Art

It is commonly understood that good glass cleaners provide various disparate characteristics within a single composition. These characteristics optimally include good detergency, acceptable evaporability, streak-resistance and  
15 the like. In view of the often contradictory nature of these features, it has proven difficult to produce a glass cleaner which attains them all.

Generally, glass cleaners are applied to soiled surfaces to loosen dirt while emulsifying oil and grease. The offending solubilized materials are thereafter wiped from the soiled surface. If the oil and grease are not completely emulsified or are  
20 not completely transferred to the wiping material, smearing occurs followed by streaking.

Phosphate detergents are known to provide acceptable cleaning for glass surfaces, however, they are generally perceived by consumers as harmful to the environment.

25 Typical prior art liquid glass cleaners also utilize a water-based system with a detergent and an organic solvent. For reasons of household safety and commercial acceptance, glass cleaners are nearly universally water-based. Water soluble organic detergents exhibit acceptable detergency, while detergent builders increase detergency by sequestering polyvalent metal ions, these inorganic builders  
30 are recognized in the art to cause filming and streaking.

Consumers are highly sensitive to streaking and hazing which may develop on windows and mirrors. A desirable glass cleaner should produce a glass surface

which exhibits little or no change in clarity and optical properties from the moment of use and ideally remain that way for weeks and months. In the context of the present invention, streaking can be defined as a visible diffractive layer which causes light scattering. Hazing can be described as a misty diffractive layer that covers the  
5 entire glass surface developing instantly or over time, which clouds the view.

Most cleaning products leave behind a thin residual film of product in intimate contact with the silicate glass. Hydrogen bonding to the surface oxides and/or hydroxides with continuous attachment produces an optically clear film. Small breaks or disruptions in these continuous residual films cause diffractive  
10 streaks which are visible to the naked eye. Similarly, residual diffractive particles will also be visible to the naked eye. Specific formulation techniques are required to maintain the integrity of a homogeneous residual film and to eliminate residual diffractive particles on the cleaned glass surface.

Chemical and optical stability of the residual surface film may be achieved by  
15 maintaining a proper balance of surfactants and coupling agents in the formula. More typically, however, the formulator will prepare a cleaning composition to ensure stability of the composition and the delivery of good detergency without considering the residual film properties and optical effects.

Formulating to improve residual film properties requires knowledge of the  
20 formula composition during the dry down process. The volatility of the individual components and their surface interactions as they evaporate at different rates also need to be considered. For example, the addition of n-hexanol to a low solvent amphoteric-based glass cleaner will reduce its propensity to streak and haze since n-hexanol couples well with the residual surfactants and the silicate surface.

25 Nonvolatile glycol ether-based cleaning formulas represent a completely different coupling problem. Cleaning compositions containing nonvolatile glycol ethers, such as hexyl cellosolve (ethylene glycol n-hexyl ether) or butyl cellosolve (ethylene glycol n-butyl ether) represent a different situation because hexyl cellosolve and butyl cellosolve are less soluble and less volatile than other formula  
30 components. For example, during the dry down process, each of these materials

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tends to complex with itself, thereby forming small diffractive particles which pull away from the glass and create the phenomenon known as streaking. The breaking of the solid-liquid interface to form small droplet-like particles of hexyl cellosolve or butyl cellosolve occurs with the preferential loss of the coupling agent and total  
5 energy.

Applicants have discovered that a glass cleaning composition containing ethylene glycol n-butyl ether is virtually streak free because the glycol ether is coupled with a fluoro surfactant and isopropanol to set up the proper cure and dry down integrity. However, this composition is not as easy for a consumer to use  
10 because it does not reduce the lateral or "rub-out" friction created between the cleaning implement such as a paper towel and the glass surface during the cleaning process.

U.S. Patent No. 3,839,234 relates to cleaning compositions comprising a glycol ether, a glycol, a monohydroxy alcohol, an amine and a synthetic detergent.  
15 The synthetic detergent, which is not derived directly from fat or oils, volatilizes and does not leave significant films or detergent residue on surfaces.

U.S. Patent No. 3,939,090 relates to cleaning compositions comprising a lower alkylene glycol, a lower alkyl monoether such as ethylene glycol monobutyl ether or propylene glycol monomethyl ether and an aliphatic alcohol. Exemplified  
20 alcohols are isopropanol, butanol and ethanol.

U.S. Patent No. 4,315,828 relates to aqueous glass cleaning compositions containing polyethylene glycol or methoxypolyethylene glycol to provide a coating on the glass to repel the emulsified oil and grease, thereby enhancing its transfer to the toweling and providing a streakless cleaner.

25 U.S. Patent No. 5,108,660 relates to aqueous glass cleaning compositions containing a hydrocarbyl-amidoalkylene sulfobetaine detergent surfactant to reduce streaking and filming.

#### **Brief Description of Drawings**

Figure 1 illustrates the surface wetting properties attained by certain compositions according to the present invention;

Figure 2 illustrates contact angle properties attained by certain compositions according to the present invention;

5 Figure 3 illustrates mean film thickness profiles of glass surfaces treated with glass cleaning compositions of the present invention and the prior art; and

Figures 4-6 illustrate the rub-out friction of glass surfaces treated with glass cleaning compositions according to the present invention and the prior art.

It is an object of the present invention to provide cleaning compositions with  
10 good streak-resistance.

This object and other objectives are provided by a novel aqueous composition which comprises a nonvolatile glycol ether and an anti-streaking alcohol.

## 15 Disclosure of Invention

The above features and advantages are provided by the present invention of an aqueous cleaning composition comprising a combination of at least one nonvolatile organic ether compound and at least one anti-streaking alcohol compound. If desired, these compositions may also contain one or more of the  
20 following: an amphoteric surfactant, a quaternary compound, an organic solvent, coloring and fragrance. The composition may also contain other conventional materials including, but certainly not limited to; ammonia, vinegar, chelating agents, pH modifiers, hydrotropes, anti-microbial compounds, etc.

In order to attain good soil agglomeration, the present invention contains at  
25 least one nonvolatile organic ether. The nonvolatile organic ethers according to the present invention are represented by the following Formula (I):



wherein  $R_1$  is a  $C_1$ - $C_8$  linear, branched or cyclic alkyl or alkenyl optionally substituted with  $-OH$ ,  $-OCH_3$ , or  $-OCH_2CH_3$  and  $R_2$  is a  $C_1$ - $C_6$  linear, branched or  
30 cyclic alkyl or alkenyl substituted with  $-OH$ .

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Preferably,  $R_1$  is an optionally substituted  $C_3$ - $C_6$  alkyl or alkenyl, and  $R_2$  is a monosubstituted  $C_2$ - $C_4$  linear or branched alkyl or alkenyl.

More preferably,  $R_1$  is an unsubstituted or monosubstituted linear or branched  $C_3$ - $C_6$  alkyl, and  $R_2$  is a monosubstituted  $C_2$ - $C_4$  linear or branched alkyl.

5 Most preferably,  $R_1$  is an unsubstituted  $n$ - $C_3$ - $C_4$  or  $n$ - $C_6$  linear alkyl or  $-CH_2CHCH_3$ , and  $R_2$  is  $-CH_2CH_2OH$  or  $-CH_2CHCH_3$ .



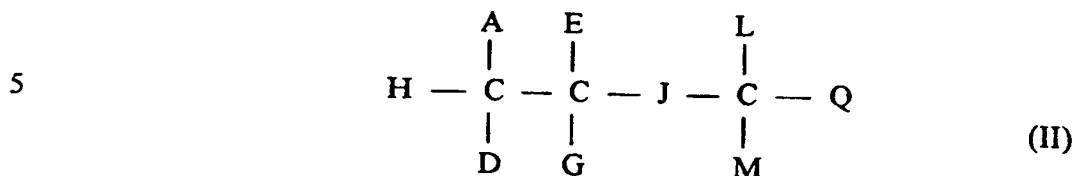
Suitable nonvolatile glycol ethers include ethylene glycol  $n$ -hexyl ether,  
 10 ethylene glycol  $n$ -butyl ether, dipropylene glycol methyl ether, propylene glycol  $n$ -butyl ether and propylene glycol  $n$ -propyl ether. However, since ethylene-based glycol ethers may be considered hazardous in the future and/or environmental air pollutants based on their degradation products or toxicity, the propylene-based glycol ethers may be better suited for residential cleaning compositions, particularly  
 15 when intended for indoor use. One commercially available non-volatile glycol ether is Dow Triad which is an equal weight percentage mixture of dipropylene glycol methyl ether, propylene glycol  $n$ -butyl ether and propylene glycol  $n$ -propyl ether commercially available from Dow Chemicals.

In the present invention, the nonvolatile glycol ether(s) can be contained in  
 20 any amount desired. Generally, these amounts will be selected to achieve good cleaning results and are commonly in the range from about 0.1 to about 5.0 total weight percent (hereinafter, all amounts are given in weight percent unless specified otherwise). Preferably, the nonvolatile glycol ether is employed in the range from about 0.5 to about 3.0 total weight percent and most preferably, from about 0.9 to  
 25 about 2.5 total weight percent.

This invention relates to the discovery that certain alcohols couple with the nonvolatile organic ethers and markedly reduce the potential of glass cleaning compositions to develop visible streaks as well as to enhance the ease of use by the consumer. These anti-streaking alcohols include various monohydric alcohols,  
 30 dihydric alcohols, trihydric alcohols and polyhydric alcohols.

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The anti-streaking alcohols for use in the present invention are represented by the following Formula (II):



wherein A, D, E, G, L and M are independently -H, -CH<sub>3</sub>, -OH or -CH<sub>2</sub>OH; J is a single bond or -O-; and Q is -H or a straight chain C<sub>1</sub>-C<sub>5</sub> alkyl optionally substituted with -OH, with the proviso that:

- (i) if Q is not an alkyl substituted with -OH, then at least one of A, D, E, G, L and M is -OH or -CH<sub>2</sub>OH;
- (ii) when only one of A and E is -OH and J is a single bond, D, G, L, M and Q may not be -H simultaneously;
- (iii) when A, D, E, G and L are -H simultaneously, J is a single bond and M is -CH<sub>2</sub>OH, Q may not be -H or -CH(OH)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>; and
- (iv) when J is single bond, none of E, G, L and M is -CH<sub>3</sub> or -CH<sub>2</sub>OH and Q is -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, then at least two of A, D, E, G, L and M are -OH; or at least one of A and D is -CH or -CH<sub>2</sub>OH.

Preferably, at least one of A, D, E and G is -OH or -CH<sub>2</sub>OH and Q is -H or a straight chain C<sub>1</sub>-C<sub>5</sub> alkyl optionally monosubstituted with -OH.

More preferably, one or two of A, D, E and G is -OH or -CH<sub>2</sub>OH and Q is -H or -CH<sub>2</sub>OH.

Most preferably, one or two of A, D, E and G is -OH or -CH<sub>2</sub>OH, J is -O-, L and M are independently -H or -CH<sub>3</sub> and Q is -CH<sub>2</sub>OH.

The inventors have found that propylene glycol (1,2-propanediol), glycerin (1,2,3-propanetriol), n-hexanol, 1-pentanol, 2-pentanol, 3-pentanol, 1,3-butylene glycol (1,3 butanediol) and diethylene glycol (dihydroxy diethyl ether) function especially well to adequately couple the nonvolatiles.



Other alcohols were found functionally not to reduce streaking characteristics. These include 2-ethyl-1,3-hexanediol, 2,2,4-trimethyl-1,3-pentanediol, 1-heptanol, 2-heptanol and 3-heptanol.

The inventors have observed that the properly coupled cleaning  
5 compositions facilitate soil removal with minimum soil redeposition. Nonvolatile organic ether-based formulas have the tendency to form stable agglomerates which may not preferentially absorb into the cleaning towel substrate. Maintaining the proper surface energy with stable alcohol solutions maximizes soil pick up and deposition on the towel substrate with a minimum of redeposition on the solid  
10 surface.

In the present invention, the anti-streaking alcohol(s) will be employed in any desired amounts. Generally, these amounts will be selected to achieve reduction in streaking and/or hazing and are commonly in the range of from about 0.1 to about 5.0 total weight percent. Preferably, the anti-streaking alcohol is  
15 employed in the range of from about 0.1 to about 3.5 total weight percent and most preferably, from about 0.2 to about 2.5 total weight percent.

Surprisingly, the amount of streak reduction provided by the anti-streaking alcohol is not a linear function with increasing amounts of anti-streaking alcohol but is instead a gaussian-shaped curve in which approximately equal parts of alcohol to  
20 the formula nonvolatiles produces the least amount of streaking.

The inventors have determined that surface wetting and contact angle are good measures of potential long term film stability for nonvolatile glycol ether containing glass cleaners. These performance indices are both measured by placing a single drop (ca. 0.04 gr. or 5 $\mu$ l, respectively) of the test product from a pipette  
25 onto an untreated mirror and/or glass surface.

Figure 1 shows a non-linear curve illustrating surface wetting measurements taken from glass cleaning compositions containing 0.9 weight percent ethylene glycol n-hexyl ether and varying amounts of propylene glycol. A control cleaning composition containing 0.9 weight percent ethylene glycol n-hexyl ether provided  
30 surface wetting spread of 21 mm.

Figure 2 shows a non-linear curve illustrating contact angle measurements taken from glass cleaning compositions containing 0.9 weight percent ethylene glycol n-hexyl ether and varying amounts of propylene glycol. A control cleaning composition containing 0.9 weight percent ethylene glycol n-hexyl ether provided a  
5 contact angle of 22°.

Figure 1 illustrates that surface wetting obtained upon application of the glass cleaner reaches a maximum when the amount of streak reducing alcohol is similar to the amount of nonvolatile glycol ether. Moreover, Figure 2 also illustrates that the contact angle obtained upon application of the glass cleaner  
10 reaches its minimum when the amount of streak reducing alcohol is approximately the same as the amount of nonvolatile glycol ether. Without being bound by this explanation, the inventors believe it is most effective to formulate the glass cleaner so as to maximize the average spread while minimizing the contact angle.

The glass cleaning compositions according to the present invention may  
15 contain one or more surfactants to adjust the surface tension of the composition. These surfactants may preferably include cationic fluoro surfactants such as 3M Fluorad® FC-135, anionic surfactants such as decyl (sulfophenoxy) benzenesulfonic acid disodium salt sold by Dow Corp. as Dowfax® C10L or amphoteric surfactants such as caprylic glycinate sold by Witco Corp. as Rewoteric® AMV. The anionic  
20 surfactant may also be a fluoro anionic surfactant such as 3M Fluorad® FC-129. Other suitable surfactants include betaine surfactants such as coco amido propyl dimethyl sultaine sold by Lonza Corp. as Lonzaine® CS, coconut based alkanolamide surfactants sold by Mona Chemicals as Monamid® 150-ADD or ethoxylated alcohols such as Neodol® 23-3 (Shell Chemicals), low foaming  
25 surfactants such as lauramine oxide sold by Lonza Corp. as Barlox® LF and cleaning surfactants such as ethoxylated vegetable oil sold by GAF Corp. as Emulphor® EL-719.

Generally, the inventors have found that the use of cationic amphoteric surfactants may result in glass cleaners which have a tendency for streaking or  
30 smearing problems. Accordingly, amphoteric surfactants used in the present

invention are preferably employed under alkaline conditions to render the anionic portion of the amphoteric compound active.

Ideally, the amphoteric surfactant exhibits high detergency and low foam characteristics. Suitable examples of such amphoteric compounds include a capryloamphodipropionate such as Amphoterge® KJ-2 (Lonza Corp.) which has a lipophilic end with a chain length including the amide carbon of C<sub>6</sub> (4%); C<sub>8</sub> (57%); C<sub>10</sub> (38%) and C<sub>12</sub> (1%).

The amphoteric surfactants may desirably be utilized in their salt-free forms to maximize their compatibility in the glass cleaning systems; particularly if the glass cleaner contains detergents.

In the present invention, the surfactant(s) will be employed in the range from 0 to about 5.0 weight percent, preferably in the range of from about 0.01 to about 3.0 weight percent and most preferably in the range of from about 0.01 to about 2.0 weight percent.

The glass cleaning compositions according to the present invention may also contain a quaternary compound which enhances the anti-fog activity of the amphoteric surfactant. Such compounds include any conventional quaternary ammonium salt compound in which a positively charged central nitrogen atom is joined to four organic groups associated with a negatively charged acid radical. The quaternary compounds are also intended to include other positively charged tetravalent nitrogen atom salts, including betaines and sulfobetaines. Preferable quaternary compounds include an ethyl bis (polyethoxy ethanol) such as Variquat® 66 and K-1215 from Witco Corp. Variquat® 66 and K-1215 are known generically as tallow ammonium chloride.

Typically, glass cleaning compositions prepared in conformity with this invention will contain from 0 to about 2.0 weight percent quaternary compound, preferably from about 0.075 to about 1.0 weight percent quaternary compound and most preferably, from about 0.1 to about 0.75 weight percent quaternary compound.

The glass cleaning compositions may also provide anti-microbial and/or disinfectant compounds including quaternary ammonium compounds, such as alkyl dimethyl benzyl/dialkyl dimethyl ammonium chloride sold by Lonza Corp. as Bardec® 208M. The formulator may also choose to include one or more cleaning  
5 solvents or cleaning supplements such as monoethanolamine. These cleaning solvents will typically be utilized in amounts from 0 to about 2.0 weight percent, preferably from about 0.01 to about 1.0 weight percent and most preferably, from about 0.125 to about 0.8 weight percent.

The glass cleaning compositions according to the present invention may also  
10 contain cleaning aids such as sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ), which is useful for improving the removal of various types of stains and penetrating soils, or gluconic acid ( $\text{HOCH}_2(\text{CH}(\text{OH}))_4\text{CO}_2\text{Na}$ ), which improves cleaning, provides sequestering, and promotes rust removal. These cleaning aids will typically be utilized in amounts of from 0 to about 1.0 weight percent, preferably from about 0.01 to about 0.80  
15 weight percent and most preferably, from about 0.1 to about 0.5 weight percent.

For better consumer acceptance, the glass cleaning composition will typically contain colorant or dye, such as Direct Blue 86, Liquitint® or Blue HP and a fragrance component. If a dye or a fragrance is contained in the composition, it may be preferable also to include an anti-oxidant, such as potassium iodide, to  
20 protect these materials and provide sufficient stability for a long shelf life. Of course, it is certainly possible for commercial or other reasons to provide a clear or fragrance-free composition by omitting these materials.

Compositions of the present invention may have any desired pH. However, preferred compositions according to the present invention are basic in order to  
25 cause any amphoteric surfactant which may be present to become more anionic and more hydrophilic. Of course, the particular pH selected may depend greatly upon any individual surfactant which is utilized. Generally, however, the pH of the composition is above 7, more preferably from 8-13 and ideally from 10-11.

MODES OF CARRYING OUT THE INVENTION

The following compositions are either Illustrative Examples of various representative embodiments of the present invention or Comparative Examples thereof.

Example 1

An anti-streak glass cleaning composition according to the present invention was prepared according to the following formula:

10	Sodium dodecyl benzene sulfonate	0.2000
	Monoethanolamine	0.2000
	Ethylene glycol n-hexyl ether	0.9000
	Ethylene glycol n-butyl ether	1.0000
15	Isopropyl alcohol	4.2500
	1,3-Butylene glycol	0.7500
	Anionic fluoro surfactant	0.0250
	Fragrance	0.0500
	Potassium iodide	0.0030
20	Dye	0.0007
	Ammonia (28.5% active)	0.3000
	Deionized water	balance

Example 2

An anti-streak disinfecting glass cleaning composition according to the present invention was prepared according to the following formula:

5	Lauramine oxide	0.4000
	Glycerin	0.2000
	Alkyl dimethyl benzyl/dialkyl dimethyl ammonium chloride (80% active)	0.1200
	Monoethanolamine	0.4000
10	Hexanol	0.3000
	Isopropyl alcohol	2.5000
	Propylene glycol n-butyl ether	0.2500
	Cationic fluoro surfactant	0.0500
	Fragrance	0.0500
15	Deionized water	balance

Example 3

An anti-streak glass cleaning composition according to the present invention was prepared according to the following formula:

20	Decyl (sulfophenoxy) benzenesulfonic acid disodium salt	0.1500
	Monoethanolamine	0.2000
	Ethylene glycol n-hexyl ether	0.6000
	Ethylene glycol n-butyl ether	0.8000
25	Isopropyl alcohol	3.5000
	Anionic fluoro surfactant	0.0250
	Fragrance	0.0500
	Propylene glycol	0.2500
	Dye	0.0014
30	Ammonia (28.5% active)	0.3000
	Soft water	balance

Example 4

An anti-streak glass cleaning composition according to the present invention was prepared according to the following formula:

5	Sodium dodecyl benzene sulfonate	0.2000
	Monoethanolamine	0.2000
	Ethylene glycol n-hexyl ether	0.7000
	Ethylene glycol n-butyl ether	0.5500
	Isopropyl alcohol	4.0000
10	Propylene glycol	1.0000
	Anionic fluoro surfactant	0.0250
	Fragrance	0.0500
	Dye	0.0014
	Ammonia (28.5% active)	0.3000
15	Soft water	balance

Example 5

An anti-streak glass cleaning composition according to the present invention was prepared according to the following formula:

20	Sodium dodecyl benzene sulfonate	0.2000
	Monoethanolamine	0.2000
	Ethylene glycol n-hexyl ether	0.7000
	Ethylene glycol n-butyl ether	0.5500
	Isopropyl alcohol	4.0000
25	Propylene glycol	1.0000
	Anionic fluoro surfactant	0.0250
	Fragrance	0.0500
	Dye	0.0014
	Sodium metasilicate, anhy	
30	drous	0.2500
	Ammonia (28.5% active)	0.3000
	Soft water	balance

Example 6

An anti-streak glass cleaning composition according to the present invention was prepared according to the following formula:

5	Sodium dodecyl benzene sulfonate	0.2000
	Monoethanolamine	0.2000
	Ethylene glycol n-hexyl ether	0.7000
	Ethylene glycol n-butyl ether	0.5500
	Isopropyl alcohol	4.0000
10	Propylene glycol	1.0000
	Anionic fluoro surfactant	0.0250
	Fragrance	0.0500
	Dye	0.0014
	$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$	0.2500
15	Ammonia (28.5% active)	0.3000
	Soft water	balance

Example 7

An anti-streak glass cleaning composition according to the present invention was prepared according to the following formula:

20	Sodium dodecyl benzene sulfonate	0.2000
	Monoethanolamine	0.2000
	Ethylene glycol n-hexyl ether	0.7000
	Ethylene glycol n-butyl ether	0.5500
25	Isopropyl alcohol	4.0000
	Propylene glycol	1.0000
	Anionic fluoro surfactant	0.0250
	Fragrance	0.0500
	Dye	0.0014
30	Gluconic acid	0.2500
	Ammonia (28.5% active)	0.3000
	Soft water	balance



Example 8:

A composition was prepared with the following formula:

<u>Ingredient Name</u>	<u>% w/w</u>
Isopropyl Alcohol, Anhydrous	3.500000
Ethylene Glycol Monobutyl Ether	1.000000
Ethylene Glycol N-Hexyl Ether	0.900000
Ammonium Hydroxide	0.300000
Propylene Glycol, Industrial Grade	0.250000
Sodium Dodecyl Benzene Sulfonate	0.200000
Caustic Soda, 50% Liquid	0.060000
Fragrance	0.050000
Dye	0.000700
Cationic fluoro surfactant	0.020000
Soft Water	balance

Comparative Example 1

5 A composition was prepared according to the following formula:

Sodium dodecyl benzene sulfonate	0.2000
Monoethanolamine	0.2000
Ethylene glycol n-hexyl ether	0.9000
Ethylene glycol n-butyl ether	1.0000
10 Isopropyl alcohol	3.5000
2-Ethyl-1,3-hexanediol	1.5000
Anionic fluoro surfactant	0.0250
Fragrance	0.0500
Potassium iodide	0.0030
15 Dye	0.0007
Ammonia (28.5% )	0.3000
Deionized water	balance

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Comparative Example 2

A composition was prepared according to the following formula:

	Capryloamphodipropionate	0.2500
5	Caprylic Glycinate	0.4500
	Monoethanolamine	0.4000
	Ethyl lactate	1.0000
	Ethyl bis (polyethoxy ethanol) tallow ammonium chloride	0.2000
	Cationic fluoro surfactant	0.0200
10	Fragrance	0.0600
	Dye	0.0007
	Ammonia (28.5% )	0.2200
	Deionized water	balance

15 Comparative Example 3

A composition was prepared according to the following formula:

	Capryloamphodipropionate	0.2500
	Caprylic Glycinate	0.4500
20	Monoethanolamine	0.4000
	2-ethyl-1,3-hexanediol	1.0000
	Ethyl bis (polyethoxy ethanol) tallow ammonium chloride	0.2000
	Cationic fluoro surfactant	0.0200
	Fragrance	0.0600
25	Dye	0.0007
	Ammonia (28.5% )	0.2200
	Deionized water	balance

Comparative Example 4

A composition was prepared according to the following formula:

Sodium lauryl sulfate	0.5000
5 Capryloamphodipropionate	0.6500
Ethyl bis (polyethoxy ethanol) tallow ammonium chloride	0.4500
Monoethanolamine	0.4000
Anionic fluoro surfactant	0.0250
Fragrance	0.0400
10 Dye	0.0007
Ammonia (28.5%)	0.2500
Deionized water	balance

Comparative Example 5

15 A composition was prepared according to the following formula:

Lauramine oxide	0.4000
Alkyl dimethyl benzyl/dialkyl dimethyl ammonium chloride	0.1200
Monethanolamine	0.4000
Isopropyl alcohol	2.5000
20 Propylene glycol N-butyl ether	0.2500
Cationic fluoro surfactant	0.0500
Fragrance	0.0500
Deionized water	balance

Comparative Example 6

A composition was prepared according to the following formula:

	Capryloamphodipropionate	0.2500
5	Caprylic glycinate amphoteric surfactant	0.4500
	Ethyl bis (polyethoxy ethanol) tallow ammonium chloride	0.2000
	Monoethanolamine	0.4000
	Anionic fluoro surfactant	0.0200
	Fragrance	0.0500
10	Dye	0.0004
	Ammonia (28.5%)	0.2200
	Deionized water	balance

Comparative Example 7

15 A composition was prepared according to the following formula:

	Sodium dodecyl benzene sulfonate	0.2000
	Monoethanolamine	0.2000
	Ethylene glycol N-hexyl ether	0.9000
	Ethylene glycol N-butyl ether	1.0000
20	Isopropyl alcohol	5.0000
	Anionic fluoro surfactant	0.0250
	Fragrance	0.0500
	Potassium iodide	0.0030
	Dye	0.0014
25	Ammonia (28.5%)	0.3000
	Soft water	balance

Comparative Example 8:

A composition was prepared according to European Patent Application No. 0527625A2:

5	Sodium lauryl sulfate (30%)	0.34364
	Isopropyl alcohol, anhydrous	2.76000
	Ethylene glycol-N-butyl ether	1.74000
	Low molecular weight polyacrylic acid	0.04200
	Anionic fluoro surfactant	0.01500
10	Fragrance	0.02000
	Dye	0.00070
	Ammonia (28.5%)	1.0000
	Soft water	balance

15 EVALUATION

Glass cleaning compositions are evaluated directly for streaking and hazing by actual use and observation. The streaking/hazing potential of a glass cleaner is evaluated by observing a mirror with direct illumination using bright (300 W/Btu  
20 880) light. While windows and glass panels can also be used to evaluate application performance, angle of view and lighting techniques become more critical. A problem glass cleaner may instantly streak or develop a haze within a few days. These problems can be further complicated by the cleaning process, cleaning towel and specific soil types encountered.

25 For evaluation by direct observation, mirrors are prepared by cleaning with HPLC grade acetone and wiped with an AccuWipe™ (Fort Howard) or Cheesecloth Wipe™ (VWR). This acetone wash is followed by cleaning with ethanol and a Cheesecloth Wipe™ and dried thoroughly.

- 20 -

Equal amounts of the test products are applied to the prepared mirror surfaces by trigger or aerosol spray or are applied uniformly with an eye dropper at the rate of approximately 1 ml per 6" x 12" (15.2 cm x 30.5 cm) area.

A folded paper towel is used to rub out the liquid test product with three to  
5 four up-and-down strokes followed by two cross strokes. The paper towel is then turned over and its clean side is used in a vertical stroke until the glass is coated with a consistent wet film which is allowed to air dry (referred to in the results as "Wet") or until the glass is completely dry and bright (referred to in the results as "Dry"). Immediately after application, the mirror is observed under a bright  
10 spotlight and any streaking is recorded. The mirror is then stored vertically in a controlled test room which is free of chemical and particulate contamination. The mirror is examined periodically for haze development and any other changes at an observation sequence of approximately one hour, 24 hours and then weekly for a period of two months. The treated surfaces are examined with the naked eye for  
15 qualitative assessment and with video observation for quantitative evaluation under various light source conditions.

Good products will not streak or haze initially or even after 1 to 2 months under normal conditions. Inferior formulations may streak immediately or with time develop undesirable hazing.

20 The formulations of all the preceding examples, except Example 8, were evaluated using the foregoing direct observation procedure. The results are illustrated in Table 1 below. In Table 1, streaking and hazing are evaluated on a scale of 1-10, with 1 being optimum (no streaking or hazing) and 10 being the worst possible (immediate streaking or severe hazing).

25

TABLE 1

	DRY (avg.)	WET (avg.)
Example 1	1.5	6.3
Example 2	2.0	5.3
Example 3	1.3	2.3
Example 4	1.0	2.7
Example 5	2.0	3.0
Example 6	4.0	5.0
Example 7	2.0	2.0
Comparative Ex. 1	4.3	9.3
Comparative Ex. 2	4.7	8.0
Comparative Ex. 3	2.7	7.3
Comparative Ex. 4	3.0	5.0
Comparative Ex. 5	4.0	7.0
Comparative Ex. 6	2.7	4.7
Comparative Ex. 7	1.3	4.0
Comparative Ex. 8	2.0	2.5

**Stain-lifting**

The thickness of surface layers of soil material on solid substrates before and  
5 after application of a cleaning composition can be determined using the technique of  
ellipsometry. In this technique, circularly polarised, monochromatic light is used to  
illuminate the target surface and the reflected beam's polarisation is determined  
using either a Kerr cell detector or a Nicol prism system. The ellipticity of the

reflected beam is then used to calculate the thickness of the surface film from a knowledge of the incident beam's angle of incidence; and the film and substrate refractive indices. Using a computer-controlled X-Y stage, the incident beam can be tracked across the test-piece surface and the thickness profile of the surface film  
5 assessed. Such thickness profiles are a measure of the level of soil remaining on the substrate surface after cleaning.

#### Model Soil

A model soil was prepared according the following formula:

	37:63 mixture of Norpar 5/Norpar 7	98.5%
10	Synthetic sebum	0.5%
	Clay	0.5%
	Technical white oil	0.5%

#### Soiling Procedure

Cleaned glass plates (6" x 6") were evenly coated with the model soil so as  
15 to achieve a soil loading of 92 mg/sq. in. The soiled plates were left in a fume cupboard overnight to dry.

The following glass cleaning compositions were evaluated:

#### Comparative Example 9:

The following composition was prepared:

Ethylene Glycol N-Hexyl Ether	0.9000
Ethylene Glycol Monobutyl Ether	1.0000
Isopropyl Alcohol, Anhydrous	5.0000
Potassium Iodide	0.0030
Sodium Dodecyl Benzene Sulphonate (20% active)	0.4000
Monoethanolamine	0.4000
Anionic Fluoro surfactant	0.0250
Acetic Acid (80%)	0.0375
Fragrance	0.1000
Ammonia (28.5%)	0.3528
Deionized Water	balance



Example 9:

The following composition was prepared:

Isopropyl Alcohol, Anhydrous	3.5000
Ethylene Glycol n-Butyl Ether	0.8000
Ethylene Glycol n-Hexyl Ether	0.6000
Propylene Glycol	0.2500
Decyl (sulfophenoxy) benzenesulfonic acid disodium salt	0.1500
Monoethanolamine	0.2000
Ammonium Hydroxide	0.3000
Cationic fluoro surfactant	0.0250
Fragrance	0.0500
Dye	0.0014
Soft Water	balance

5 Formula 409® Glass & Surface:

A commercial formula under the tradename Formula 409® from the Clorox Co. was analyzed and is believed to have the following composition:

Isopropanol	5.4
Propylene Glycol t-Butyl Ether	4-5%
Ammonium Hydroxide	Present
Cocoamidopropyl Betaine	0.26
Water, Dye and Fragrance	Approx. 90%

10 Cleaning Procedure

The various glass cleaning samples were loaded into separate trigger spray applicators that have been checked to ensure that they delivered approximately the same amount of product per activation. Each sample was then used to treat a soiled plate using one full trigger activation to cover the whole plate surface. The treated 15 plates were then left for 30 seconds and cleaned using a Gardner Apparatus. This

cleaning involved wrapping a standard paper towel around a 60 mm x 30 mm x 90 mm wooden block. Each treated plate was then placed in the cleaning tray on the Gardner Apparatus and run for five cycles.

## 5 Ellipsometric Measurement

A purpose-built scanning ellipsometer (courtesy of B.P. Research) with a Spectra Physics He/Ne circularly polarised laser source and a Kerr cell type detector was used to determine the residue profiles, as represented by the mean film thickness profile across the glass substrate of the remaining residue after cleaning.

10 These graphs represented in Fig. 3 correspond to the results obtained during the ellipsometric scan of a cleaned 60 mm x 10 mm on the glass plate.

The residue profiles shown in Fig. 3 represent Example 9 of the present invention, Comparative Example 9, and Formula 409® Glass and Surface.

### Results

15 Fig. 3 shows the average thickness profiles for the five products tested, namely Comparative Example 9; Example 9 of the present invention; and Formula 409® Glass and Surface.

As clearly shown, the residual film on the Example 9 treated plate is less than that found on the plates treated with the other non-phosphate containing  
20 compositions. The overall ranking of the compositions on the basis of average film thickness across the plate is Example 9 < Comparative Example 9 < Formula 409 Glass and Surface.

It is important to note that a combination of film thickness and film furrowing (shown by point deviation on the graph) actually causes streaking. As a  
25 consequence, Example 9 composition containing propylene glycol does not streak to the same extent as the Formula 409® Glass and Surface Cleaner without propylene glycol. This can be confirmed by visual assessment.

**Ease of Use:**

Applicants have found that the formulations of the present invention enhance the ease of use by the consumer due to a reduction in the rub-out friction between the cleaning implement and the surface. This reduction in rub-out friction can be demonstrated using a Precision Force Scrubber from the ADAM Instrument Co..

The Precision Force Scrubber is a computer controlled mechanical scrubbing and polishing device designed to apply a fixed normal force while monitoring the frictional force throughout the scrubbing action. The number of scrubbing cycles, the acceleration and velocity of the applicator head are displayed and controlled by a graphical display interface. Data gathering and analysis software are provided to allow characterization of the applied forces throughout each back and forth scrubbing stroke and during multiple stroke cycles. Thus, cleaning, polishing, stripping and other such procedures performed by consumers can be reproducibly controlled and sensitively monitored.

The normal force is the downward force applied by the scrubber head. The lateral force represents the forces of friction between the stationary glass mirror and the moving scrubbing towel. This lateral force is also known as "rub-out" friction. The presence of an undesirable high coefficient of static friction or "tack" is represented graphically by a peak in the lateral force graph.

The controlled scrubber head was equipped with two 2" by 4" scrubbers. Strips of 1.5" wide of cotton cleaning cloth were attached to each scrubber head. The machine settings were as follows: normal force was set to 2.5 lbs; velocity 10, acceleration and deceleration 100; 20 back and forth scrubbing cycles with a 6" stroke. Approximately 0.5 grams of each test product (Example 8 and Comparative Example 7) were placed in front of each cleaning pad. This set up provides a machine controlled direct comparison of test products on a standard 12" square glass mirror.

To illustrate the enhanced reduction in rub-out friction of the present invention containing anti-streaking alcohol versus compositions without the anti-streaking alcohol, lateral force (lbs) data from the Precision Force Applicator was plotted against time (sec) as shown in Figs 4 -6.

5        Figure 4 illustrates the rub-out friction for Example 8 of the present invention (plot 1) versus Comparative Example 7 (plot 2 ) for about 12 cycles between 0 and 17 seconds. Figure 5 illustrates a comparison between the Example 8 of the present invention (plot 1 ) and Comparative Example 7 (plot 2), of the rub-out friction for 3 cycles between 15 and 19 seconds. As clearly demonstrated in  
10 Figs. 4 and 5, the composition with an anti-streaking alcohol achieved about 0.5 lb reduction in rub-out friction as compared to the composition without an anti-streaking alcohol.

Fig. 6 illustrates the rub-out friction for Example 9 of the present invention containing propylene glycol (plot 3) versus Comparative Example 8 without  
15 propylene glycol (plot 4). The test was conducted as described above, with the following exceptions: a 2" by 4" portion of a commercially available paper towel under the tradename Bounty® from the Procter & Gamble Co. was attached to each scrubber head; 1.5 ml of each test product was placed on each paper towel; and 5.0 lbs of normal force was set on the Precision Force Applicator.

20        As shown in Fig. 6, the Example 9 composition containing propylene (plot 3) exhibited less rub-out friction and less pronounced tack peaks on the glass mirror as compared to the Comparative Example 8 formulation without an anti-streaking alcohol (plot 4).

#### Industrial Applicability

25        A glass cleaning composition that provides good detergency and streak-resistance can be prepared from the cleaners of the present invention.

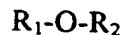
Although the present invention has been illustrated with reference to certain preferred embodiments, it will be appreciated that the present invention is not limited to the specifics set forth therein. Those skilled in the art will readily  
30 appreciate numerous variations and modifications within the spirit and scope of the

- 27 -

present invention, and all such variations and modifications are intended to be covered by the present invention which is defined by the following claims.

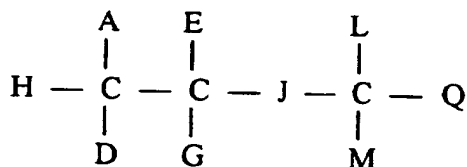
**I CLAIM:**

1. A composition for cleaning glass, comprising:  
 water;  
 a nonvolatile organic ether having the formula



wherein  $R_1$  is a  $C_1$ - $C_8$  linear, branched or cyclic alkyl or alkenyl optionally substituted with -OH, and  $R_2$  is a  $C_1$ - $C_6$  linear, branched or cyclic alkyl or alkenyl substituted with -OH; and

an anti-streaking alcohol having the formula



wherein A, D, E, G, L and M are independently -H, -CH<sub>3</sub>, -OH or -CH<sub>2</sub>OH; J is a single bond or -O-; and Q is -H or a straight chain or branched  $C_1$ - $C_5$  alkyl optionally substituted with -OH, with the proviso that:

- (i) if Q is not alkyl substituted with -OH, then at least one of A, D, E, G, L and M is -OH or -CH<sub>2</sub>OH;
- (ii) when only one of A and E is -OH and J is a single bond, D, G, L, M and Q may not be -H simultaneously;
- (iii) when A, D, E, G and L are -H simultaneously, J is a single bond and M is -CH<sub>2</sub>OH, Q may not be -H or -CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>; and



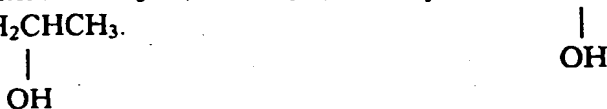
- 29 -

- (iv) when J is a single bond, none of E, G, L and M is  $-\text{CH}_3$  or  $-\text{CH}_2\text{OH}$  and Q is  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , then at least two of A, D, E, G, L and M are  $-\text{OH}$ , or at least one of A and D is  $-\text{CH}$  or  $-\text{CH}_2\text{OH}$ .

2. The glass cleaning composition according to Claim 1, wherein  $\text{R}_1$  is an optionally substituted  $\text{C}_3$ - $\text{C}_6$  alkyl or alkenyl, and  $\text{R}_2$  is a monosubstituted  $\text{C}_2$ - $\text{C}_4$  linear or branched alkyl or alkenyl.

3. The glass cleaning composition according to Claim 2, wherein  $\text{R}_1$  is an unsubstituted or monosubstituted linear or branched  $\text{C}_3$ - $\text{C}_6$  alkyl, and  $\text{R}_2$  is a monosubstituted  $\text{C}_2$ - $\text{C}_4$  linear or branched alkyl.

4. The glass cleaning composition according to Claim 3, wherein  $\text{R}_1$  is an unsubstituted  $n$ - $\text{C}_3$ - $\text{C}_4$  or  $n$ - $\text{C}_6$  linear alkyl or  $-\text{CH}_2\text{CHCH}_3$ , and  $\text{R}_2$  is  $-\text{CH}_2\text{CH}_2\text{OH}$  or  $-\text{CH}_2\text{CHCH}_3$ .



5. The glass cleaning composition according to any of Claims 1-4, wherein at least one of A, D, E and G is  $-\text{OH}$  or  $-\text{CH}_2\text{OH}$ .

6. The glass cleaning composition according to Claim 5, wherein one or two of A, D, E and G is  $-\text{OH}$  or  $-\text{CH}_2\text{OH}$ , and Q is  $-\text{H}$  or  $-\text{CH}_2\text{OH}$ .

7. The glass cleaning composition according to Claim 6, wherein J is  $-\text{O}-$ , L and M are independently  $-\text{H}$  or  $-\text{CH}_3$ , and Q is  $-\text{CH}_2\text{OH}$ .

8. The glass cleaning composition according to Claim 5, wherein said nonvolatile organic ether is present in the amount of from about 0.01 to about 5.0 total weight percent and said anti-streaking alcohol is present in the amount of from about 0.1 to about 5.0 total weight percent.

- 30 -

9. The glass cleaning composition according to Claim 6, wherein said nonvolatile organic ether is present in the amount of from about 0.5 to about 3.0 total weight percent and said anti-streaking alcohol is present in the amount of from about 0.1 to about 3.5 total weight percent.

10. The glass cleaning composition according to Claim 7, wherein said nonvolatile organic ether is present in the amount of from about 0.9 to about 2.5 total weight percent and said anti-streaking alcohol is present in the amount of from about 0.2 to about 2.5 total weight percent.

11. The glass cleaning composition according to Claim 8, further comprising up to about 2.0 weight percent monoethanolamine.

12. The glass cleaning composition according to Claim 9, further comprising from about 0.01 to about 1.0 weight percent monoethanolamine.

13. The glass cleaning composition according to Claim 10, further comprising from about 0.125 to about 0.8 weight percent monoethanolamine.



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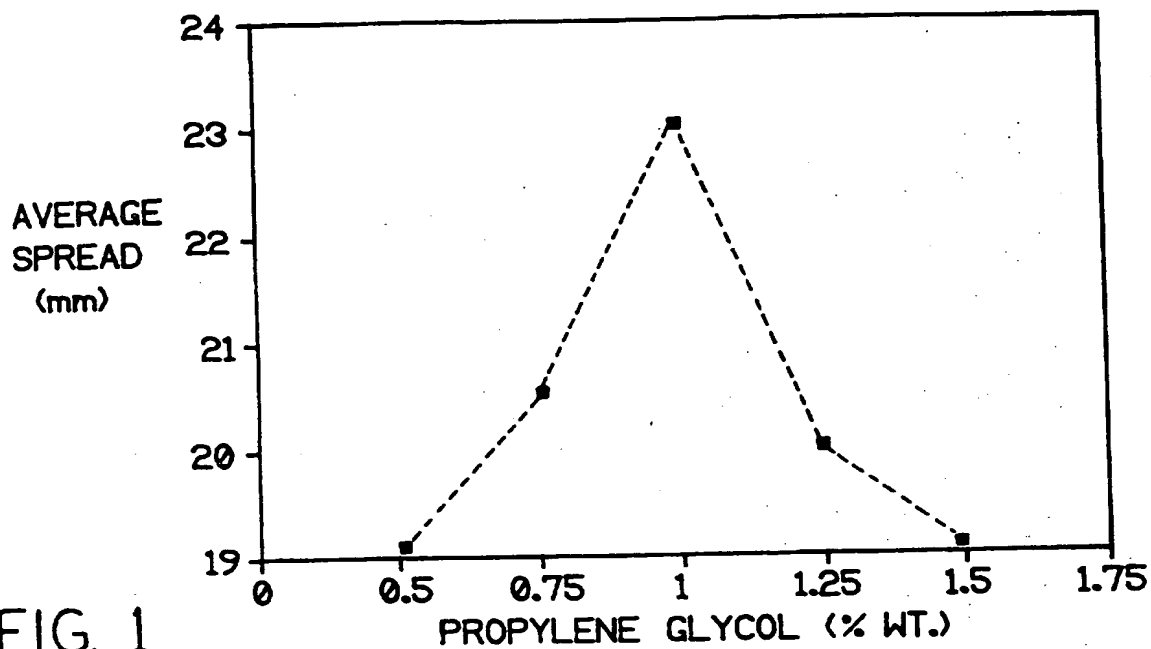


FIG. 1

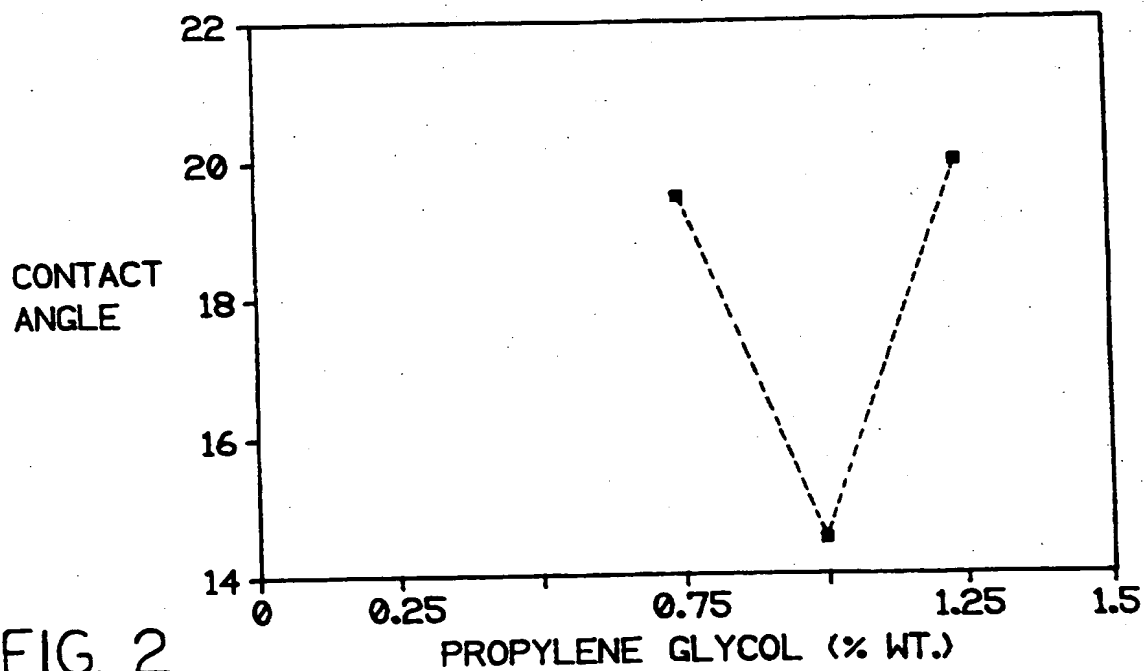


FIG. 2

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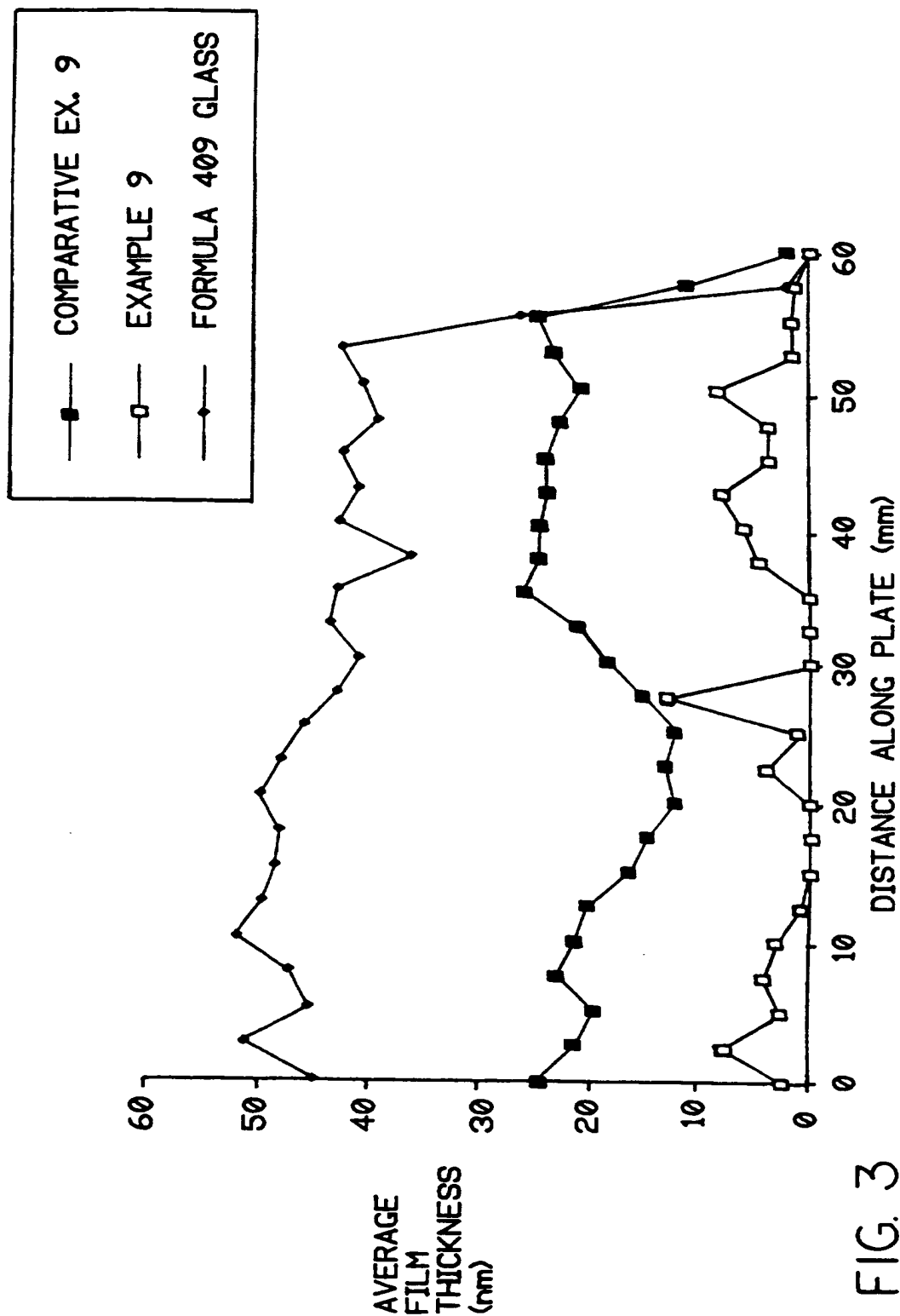
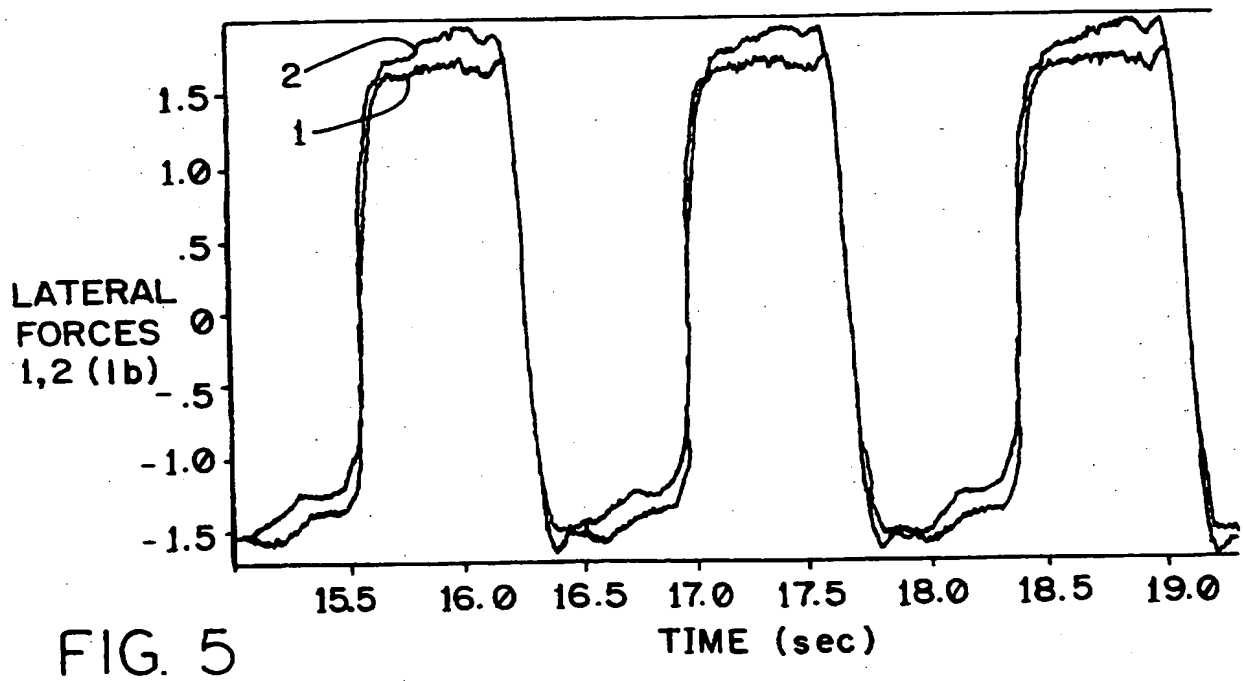
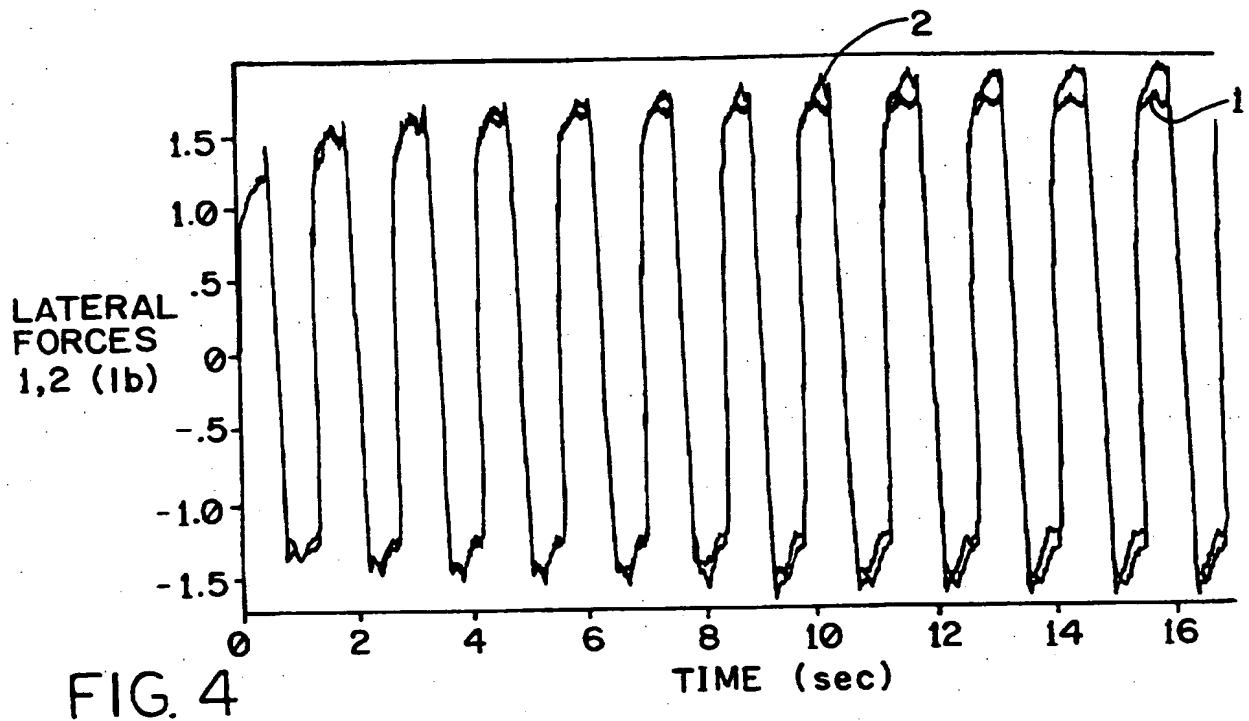


FIG. 3

3 / 4



4 / 4

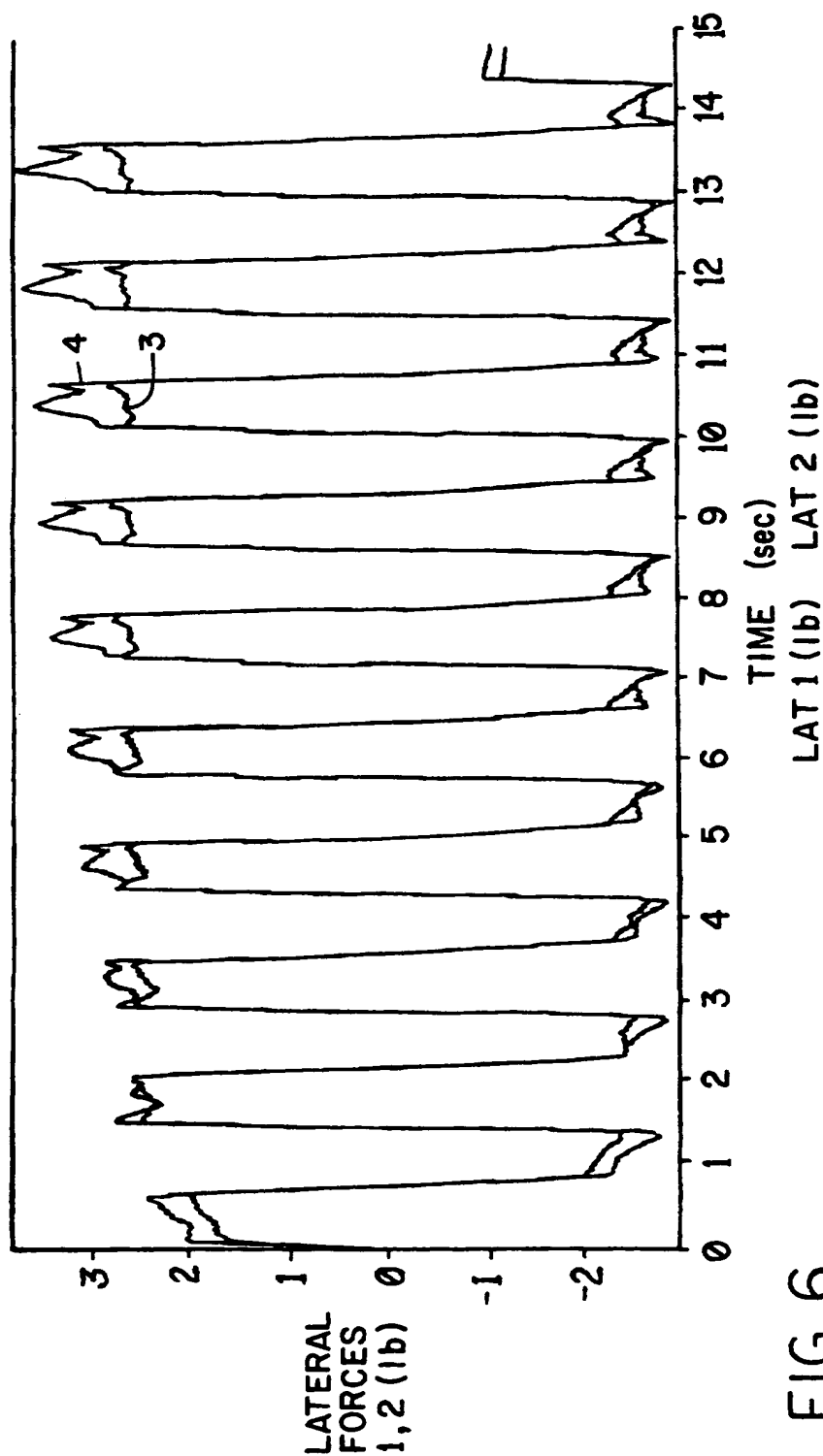


FIG. 6

# INTERNATIONAL SEARCH REPORT

Inter    nal Application No  
PCT/US 97/01654

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6    C11D3/20    C11D7/50

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6    C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 166 153 A (PROCTER & GAMBLE) 30 April 1986 see page 1, line 5-16; claims; examples ---	1-6,8-10
X	EP 0 527 625 A (SQUIBB BRISTOL MYERS CO) 17 February 1993 cited in the application see claims 1,8,11-15; examples 8,10 ---	1-6,8-10
X	US 4 302 348 A (REQUEJO LUZ P) 24 November 1981 see claim 1; examples ---	1-6,8-10
X	EP 0 647 706 A (CLOROX CO) 12 April 1995 see claims 1-3 ---	1-3,5,6, 8-10
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

3 June 1997

Date of mailing of the international search report

16-06-1997

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/01654

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 606 842 A (KEYES GEORGE B ET AL) 19 August 1986 see claim 1; examples ---	1-6,8-10
X	US 5 415 811 A (WILE RAYMOND G ET AL) 16 May 1995 see claims 1-4,6 ---	1-4,8
X	DATABASE WPI Section Ch, Week 7826 Derwent Publications Ltd., London, GB; Class A26, AN 78-46701A XP002032193 & JP 53 056 203 A (LION FAT & OIL CO LTD) , 22 May 1978 see abstract -----	1,11

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/01654

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2166153 A	30-04-86	NONE	
EP 0527625 A	17-02-93	AU 653617 B AU 2085192 A CA 2075168 A,C JP 5302099 A NZ 243831 A ZA 9205727 A	06-10-94 11-02-93 10-02-93 16-11-93 26-10-94 10-03-93
US 4302348 A	24-11-81	AU 540606 B AU 7425081 A CA 1158521 A GB 2084175 A,B JP 57085897 A	29-11-84 01-04-82 13-12-83 07-04-82 28-05-82
EP 0647706 A	12-04-95	US 5468423 A CA 2133889 A CN 1106454 A PL 305351 A US 5523024 A ZA 9407821 A	21-11-95 09-04-95 09-08-95 18-04-95 04-06-96 25-05-95
US 4606842 A	19-08-86	AU 563407 B AU 1130983 A CA 1204361 A	09-07-87 08-09-83 13-05-86
US 5415811 A	16-05-95	NONE	

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